Entropy of solid ^{4}He: the possible role of a dislocation glass

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Solid ^{4}He is viewed as a nearly perfect Debye solid. Yet, recent calorimetry indicates that its low-temperature specific heat has both cubic and linear contributions. These features appear in the same temperature range ($T \sim 200$ mK) where measurements of the torsional oscillator period suggest a supersolid transition. We analyze the specific heat to compare the measured with the estimated entropy for a proposed supersolid transition with 1% superfluid fraction. We find that the experimental entropy is substantially less than the calculated entropy. We suggest that the low-temperature linear term in the specific heat is due to a glassy state that develops at low temperatures and is caused by a distribution of tunneling systems in the crystal. It is proposed that small scale dislocation loops produce those tunneling systems. We argue that the reported mass decoupling is consistent with an increase in the oscillator frequency as expected for a glass-like transition.

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Introduction. A supersolid is a novel state of matter that simultaneously displays both superfluidity and crystalline order. ^{4}He is thought to be a most likely candidate for the supersolid state. Recent torsional oscillator experiments by Kim and Chan [1, 2] generated renewed interest in this possibility. Pioneering work by Andreev and Lifshitz [3], Reatto [4], Chester [5], Leggett [6], and Anderson [7] laid the foundation for our thinking about this enigmatic state. Recently, Anderson et al. revisited this problem [8, 9] and latest developments, presented at a KITP workshop, are available online [10].

In addition to the work of the PSU group [1, 2], there is now an independent confirmation of the anomalous behavior of solid ^{4}He, as presented by the groups of Reppy and Shirahama[11, 12]. Both groups use torsional oscillators similar to the one by the PSU group of Chan [1, 2]. At the same time Rittner and Reppy [11] reported a history dependence of the signal, when annealing the sample, to the extent of no observation of any mass decoupling in the torsional oscillator experiment. These torsional oscillator experiments clearly indicate anomalous mechanical properties of solid ^{4}He at low temperatures. However, the relationship between the mechanical measurements and the suggested superfluidity is not direct. The most direct proof of superfluidity would be observation of persistent current. In this regard, we mention a recent experimental search for superflow by Beamish et. al. [13] that indicates no mass flow of any kind to very high accuracy. Thus, we conclude that the effect first observed by the PSU group is likely not an intrinsic property of solid ^{4}He, because it depends critically on the ^{3}He concentration and shows annealing dependence [11].

Alternatively, we suggest that many of the experimental facts seem to be consistent with a glass-like behavior of crystalline ^{4}He at temperatures $T \leq 200$ mK. For the lack of any definitive experiment, we assume that the glass in ^{4}He is formed due to dislocations. In this Letter we would like to decouple the discussion of the observed features in specific heat and torsional oscillator from the supersolidity. We will focus on two critical features reported to date by experiments: (1) the small entropy that is seen experimentally near the transition temperature. The observed entropy is at almost two orders of magnitude smaller than the expected entropy of a 1% supersolid fraction. (2) The observed linear specific heat in the *bosonic* crystal of ^{4}He, consistent with a glass.

Entropy analysis. We focus on the specific heat measurements on ^{4}He by Clark and Chan [14] which indicate a departure from the conventional T^3 specific heat behavior expected at low temperatures. Given the data, we searched for evidence of a thermodynamic phase transition to a supersolid phase, assuming a 1% concentration of condensate. The observed features in the specific heat occur in the same temperature range where a change in the period of the torsional oscillator led to the speculation of a transition to a supersolid state (see Fig. 1). A low-temperature linear term in the specific heat can be discerned. We note that a linear term in the specific heat of ^{3}He and ^{4}He crystals was observed more than 40 years ago by Heltemes and Swenson [15] and Franck [16], but not in later measurements by Edwards and Pandorf [17]. A theoretical explanation of the earlier results was given in terms of thermal vibrations of pinned dislocation segments based on the theory of Granato [18].

We now perform a general thermodynamic analysis of the measured specific heat data by Clark and Chan (see Figs. 1 and 2). This is especially attractive for the analysis as its result will not depend sensitively on the exact functional form of the specific heat $C(T)$ at low temperatures, $T \leq 100$ mK. Most of the change in the entropy, $\int^T dT' \frac{C(T')}{T'}$, which we find from the data, originates from the region of 100-400 mK. According to the torsion oscillator measurements the supposed solid to supersolid transition occurs in the temperature range 160-320 mK. The low-T entropy differences of the 760 ppm and 30 ppm samples relative to solid ^{4}He are

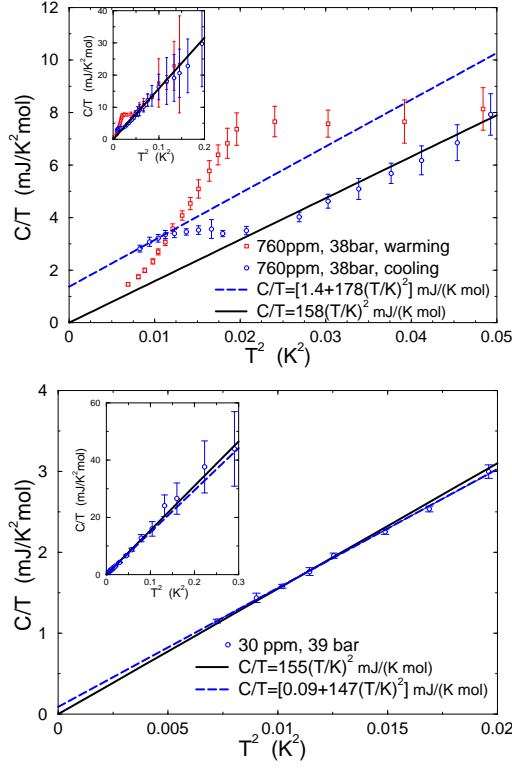FIG. 1: Specific heat over temperature of solid ^{4}He by Clark and Chan[14]. (Top): sample with 760 ppm ^{3}He at 38 bar. (Bottom): sample with 30 ppm ^{3}He at 39 bar. The dashed and solid lines are the respective low and high temperature fits, whose coefficients are presented in Table I. The insets show an enlarged temperature region.

FIG. 2: The $\Delta C/T$ differences and the corresponding entropies $\Delta S = \int_{T_{min}}^{T} dT' \Delta C/T'$ at low T. (Top): sample with 760 ppm of ^{3}He at 38 bar for cooling and warming runs; the high-T ($T > 200$ mK) contribution of solid ^{4}He, $C = B\,T^3$, with $B_{760\mathrm{ppm}} = 158$ mJ/(K^4 mol) was subtracted. (Bottom): sample with 30 ppm of ^{3}He at 39 bar; the high-T contribution with $B_{30\mathrm{ppm}} = 155$ mJ/(K^4 mol) was subtracted.

roughly $\Delta S(760\,\mathrm{ppm}) \sim 0.06 - 0.4$ mJ/(K mol) and $\Delta S(30\,\mathrm{ppm}) \sim 0.3$ mJ/(K mol) respectively, between 80 mK and 400 mK, see Fig. 2 [19].

We assume, consistent with the experimental findings, that roughly 1% of the bulk sample transforms into a superfluid. Thus 99% of the sample is unaffected and behaves like a perfect Debye crystal below ~ 500 mK ($T < \Theta_D/50$). Hence, the supersolid fraction would indicate an entropy of $S = 46$ mJ/(K mol). We now compare extracted entropy changes with what may be expected from a supersolid to solid transition (i) in a dilute gas, as suggested by a 1% supersolid component, and (ii) in a strongly correlated dense gas: (i) The Bose Einstein condensation (BEC) of an ideal gas gives values of entropy changes which are an order of magnitude larger than those observed for the λ transition of liquid ^{4}He. We follow suite here and compare the ideal BEC with that of a possible supersolid transition. Assuming a noninteracting Bose-Einstein gas in three dimensions with a parabolic band, the specific heat of the BEC is $C(T) = \frac{15}{4} \frac{\zeta(5/2)}{\zeta(3/2)} R(T/T_c)^{3/2}$ for $T \leq T_c$, with $\zeta(z)$ the Riemann zeta function and gas constant R. The total
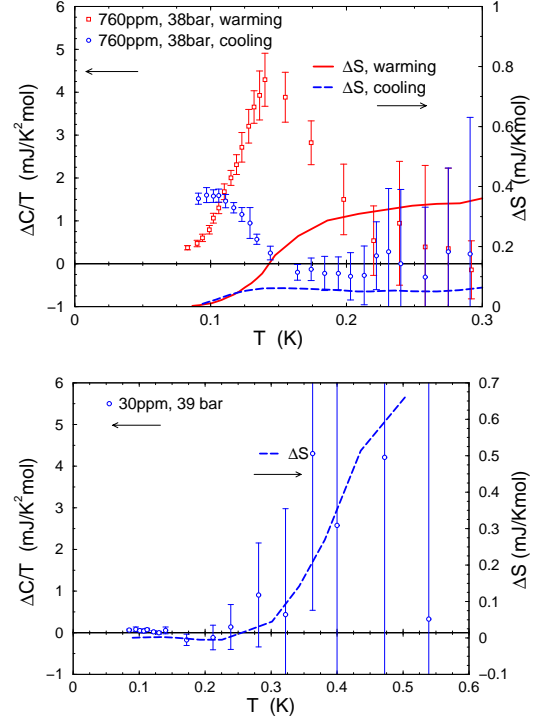
entropy per mole in the condensed state taken between $T = 0$ and T_c is universally $S_{\mathrm{BEC}}(T_c) = \frac{5}{2}\frac{\zeta(5/2)}{\zeta(3/2)} R \approx 5R$. If we use a 1% molar concentration of supersolid fraction, we still get $S_{\mathrm{BEC}}(T_c) \approx 0.05\,R = 416$ mJ/(K mol) [per mole of ^{4}He]. This is three orders of magnitude larger than the entropy changes seen in experiments (Fig. 2). These conclusions do not change if a short-range repulsive interatomic potential augments the kinetic energy in a dilute Bose gas. (ii) A lower bound can be found by scaling the measured S_λ at the λ-point of strongly correlated superfluid ^{4}He under pressure ($P_\lambda \sim 26$ bar), which is $S_\lambda = 4.6$ J/(K mol) at $T_\lambda = 1.8$ K [22]. As a generous lower bound on the entropy at an actual supersolid transition, we may correct for the fact that the claimed transition temperature is 9 times smaller (~ 200 mK for 30 ppm sample) [1] than T_λ. We scale down the expected 1% entropy by a factor of 9. Then, we may expect to find an entropy of $S_\lambda \sim 5$ mJ/(K mol). This estimate is about an order of magnitude bigger than the measured entropies. In ideal superfluids a nearly T_c independent entropy $S(T_c)$ results, even for different low-T scaling regimes, e.g., phonons, rotons. We emphasize that our

linear scaling of $S(T_c)$ is a generous lower bound [23].

More sensitive measurements of the specific heat using a new experimental setup by Chan et. al. (unpublished) are consistent with the deviations from a T^3 behavior, however, the precise form at lowest temperatures, $T \leq 80$ mK is not settled yet. Clearly, the estimated entropy associated with an actual superfluid transition is substantially larger than the measured $\Delta C/T$ integrated from ~ 80 mK to 500 mK for the case of λ transition or weakly interacting BEC. The observed deficit of entropy is very hard to reconcile with the 1% fraction of superfluid transition that is suggested to account for the torsional oscillator experiments.

A null result of the signature of a λ transition, the observation of hysteresis on cooling and warming and the dependence of the excess entropy on annealing points to a glass-like phenomenon of tunneling systems rather than that of a supersolid.

Linear specific heat and sensitivity to ^{3}He impurities. We propose that the linear specific heat term [1, 15, 16] is due to Tunneling Systems (TS) in the ^{4}He crystal. Specifically, we assume that dislocation loops are small enough to be present in large numbers ($\sim 10^{10}$cm^{-2}) to create the TS. We propose that fluctuations of nanoscale segments of dislocation loops form the TS. A small addition of ^{3}He atoms to the ^{4}He crystal facilitates the creation of dislocations; hence, the linear specific heat term should increase with ^{3}He concentration, similar to the effect of small amounts of hydrogen in crystalline tantalum [24].

The distribution of the characteristic energies of the TS is given by $P(E) = P_0 dE$, where we follow the standard discussion on the role of two-level systems in glasses [20, 21]. It is commonly assumed that at low energy P_0 is constant. We assume that P_0 is only a function of the ^{3}He concentration n_3 and any contribution from intrinsic defects in ^{4}He is neglected. ^{3}He facilitates the creation of dislocations and hence P_0 should grow with the concentration of ^{3}He. We further assume that per mole of ^{4}He, $P_0(n_3) = cN_A n_3^\nu$, with positive exponent ν and coefficient c, and Avogadro's number N_A. A natural choice is $\nu = 1$, at least for low concentrations of ^{3}He. To keep the discussion general, we will not specify ν.

The specific heat of a single tunneling system is $C_{TS}(E, T) = k_B (E/k_B T)^2 \frac{\exp(E/k_B T)}{(1+\exp(E/k_B T))^2}$. The average over the distribution of the TS gives the total molar specific heat, which at low temperatures is $C_{TS} = \int_0^\infty dE\ P(E)\ C_{TS}(E, T) \approx \frac{\pi^2}{6} k_B^2 P_0 T$. The total specific heat of ^{4}He is the sum of lattice, (C_{lat}) and the TS (C_{TS}) contributions. For a perfect Debye crystal, the molar $C_{lat} = \frac{12\pi^4}{5} R(T/\Theta_D)^3$ at low T. In solid ^{4}He, the Debye temperature $\Theta_D \approx 28$ K at $P \approx 40$ bar. Thus at low temperatures ($T \lesssim \Theta_D/50 \approx 0.5$ K) the specific heat per mole of ^{4}He is $C = AT + BT^3$, with $A = \frac{\pi^2}{6} k_B^2 P_0$ and $B = \frac{12\pi^4}{5} R/\Theta_D^3$. For $T < T^* = \sqrt{(\Theta_D^3 k_B^2 P_0)/(12\pi^2)} \sim n_3^{\nu/2}$, the linear term dominates over the lattice contribu-

TABLE I: Summary of the linear and cubic coefficients of $C = AT + BT^3$ of solid ^{4}He with ^{3}He solute, as well as its Debye temperatures Θ_D. The A is from fits below ~ 120 mK, while the B and Θ_D are from fits between 200 mK $< T \lesssim 500$ mK. Rough estimates of the uncertainties are in parentheses. For 30 ppm, A is close to zero as expected for this concentration.

| ^{3}He | P | A | B | Θ_D |
ppm	bar	mJ/(K^2 mol)	mJ/(K^4 mol)	K
30	39	0.09(4)	155(5)	23.2
760 (cooling)	38	1.4(2)	158(5)	23.1

tion. It follows that the TS model predicts that both the crossover temperature T^* and the linear coefficient A in the specific heat *will be very sensitive with respect to ^{3}He concentration.* For example, for $\nu = 1$ it leads to a square root dependence on n_3. This result also suggests that the effect of mass decoupling either vanishes or occurs at a much lower temperatures in samples with vanishing ^{3}He concentration.

We revisited the data by Clark and Chan [14], see Fig. 1, and assumed for our analysis linear and cubic terms in the specific heat. We find that indeed the data are consistent with a strong dependence on ^{3}He concentration. For example, the linear term depends on ^{3}He concentration, as shown in Table I. The A coefficient for ^{4}He reported by Heltemes and Swenson[15] and Franck[16] varied between $A \sim 2.5-8.8$ mJ/(mol K^2) at a similar pressure of $P \approx 40$ bar and with a Debye temperature $\Theta_D \approx 28$ K.[23] Their A coefficients are somewhat bigger but of the same order as ours, which are in the range of $A = 0.09 - 1.4$ mJ/(K^2 mol), depending on ^{3}He concentration and history.

The extracted low-temperature linear term coefficient A scales roughly linearly with the ^{3}He concentration. Allowing for different functional forms for the specific heat for various systems of interacting bosons does not lead to a significant change in our results.

The "missing" moment of inertia and susceptibilities. The torsional oscillator experiments measure the susceptibility - they do not directly monitor the moment of inertia of the supersolid. As in any time translationally invariant system, the Fourier amplitude of the angular response of the torsion oscillator is $\theta(\omega) = \chi(\omega)\tau_{ext}(\omega)$, with $\chi = \chi_1 + i\chi_2$ an angular susceptibility and τ_{ext} the external torque. For the simple torsional oscillator, $\chi^{-1}(\omega, T) = [\alpha - i\omega\gamma_{osc} - I_{osc}\omega^2 + g(\omega, T)]$. Here, I_{osc} is the moment of inertia of the torsional oscillator, α is its restoring constant, γ_{osc} is the dissipative coefficient of the oscillator, and $g(\omega, T)$ arises from the back action of solid ^{4}He. For an ideal normal solid with moment of inertia I_{ns}, which rotates with the oscillator, the back action is $g = -I_{ns}(T)\omega^2$. However, we do not need to impose this form. Current experiments measure the oscillator period $2\pi/\omega_0$ with ω_0 the real part of the solution of $\chi^{-1}(\omega, T) = 0$ at fixed T. For example, a decrease in an

effective dissipative component $(-i\gamma_{glass}\omega)$ in $g(\omega, T)$ as the temperature is lowered (wherein a liquid component transforms into a solid glass) will also lead to a shorter rotation period. The decrease in the rotation period only implies a crossover in χ (and a constraint on g). As the real and imaginary parts of χ are related by the Kramers-Kronig relations, an enhanced decrease in $\chi_1(\omega, T)$ often appears with a pronounced peak in χ_2 [11]. A nonvanishing χ_2 at finite frequency mandates dissipation.

The microscopic deformation of the glass to the applied torsion might, similar to suggestions [25] concerning torsional oscillator results on granular media [26], take the form of elastic, plastic, and fracture processes (including those of internal avalanches). A gradual change can proceed through dislocation glide in the slip plane [27]. All these possibilities need to be addressed experimentally before we can have a definitive microscopic picture of the possible glass state.

One way to differentiate between glassy effects and a true thermodynamic ρ_s is to measure the frequency dependence of ρ_s. For the dislocation TS that we propose, $\rho_s(T, \omega)$ will be a nontrivial function of frequency which vanishes as a power of frequency $\rho_S(T \to 0, \omega) \sim \omega^\alpha$. On the other hand, for a true supersolid phase there is a finite limit $\rho_S(T \to 0, \omega) \sim \rho_s(0)$.

Heat Pulse Experiment. A heat pulse experiment may test for the existence and relevance of the TS for the thermal properties [28]. In the absence of TS, the heat pulse would trigger quick equilibration of the energy with the phonon bath. Hence, on a very short time scale the temperature of a sample will reach a steady state value. By contrast, for a crystal with TS, the heat deposited in the crystal will first be absorbed by the phonon bath and later will cause the re-population of the TS as a result of the energy transfer from phonon bath to TS.

Conclusions. We find that the measured entropy excess is several orders of magnitude smaller than the entropy expected from the BEC or λ transition of 1% superfluid fraction. While the absence of the entropy released at claimed supersolid transition is puzzling, it is consistent with a dislocation induced glassy state in ^{4}He crystals. This hypothesis predicts that the linear term in the specific heat increases with ^{3}He concentration. Heat pulse, heat transport and ultrasound measurements would be helpful in identifying tunneling systems if they indeed exist in crystalline ^{4}He. The increase in the oscillator frequency at low temperatures is consistent with this interpretation.

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